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A TECHNICAL REVIEW OF MICROWAVE-INDUCED PLASMAS AND THEIR INDUSTRIAL APPLICATIONS

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Microwave-induced plasmas are mixtures of electrons, ions, and neutral atoms which can be produced by exposing ordinary gases to strong microwave fields. The wide variety of physical and chemical reactions which may be produced using plasmas are of growing economic importance to industry. These applications are surveyed and their relevance is evaluated. The possible role of the Utilization Section in this area is also discussed.

INTRODUCTION

In 1986, the microelectronics industry spent more than one billion US dollars worldwide on plasma-based process equipment/1/. Although this is by far the most important industry sector, many other examples of interesting and potentially important developments exist. Basically microwave plasmas can produce highly reactive conditions at low temperatures. This ability is now finding application in the chemical, ceramic, metal fabrication, and plastics industries. The purpose of this report is to review this growing electrical technology and discuss any possible involvement by the Utilization Section.

SUMMARY

This study indicates that microwave-induced plasmas are of growing importance to industry because they are cool, clean, compact and safe. This is despite technical problems with plasma non-uniformity and restricted processing volume. High capital costs, lack of off-the-shelf equipment, and the necessity of highly skilled personnel are also significant drawbacks.

The technology as a whole is generally immature, being limited to low power or small scale applications. To date, widespread use is found only when quality enhancement is important in high added-value processes. Growth is currently limited by technical difficulties rather than technology transfer. The potential for future large scale use in the chemical or paper industries exists.

At the present time, it seems that any involvement by the Utilization Section should be in process development. Sintering of advanced ceramics, or sputtering of coatings on windows are possible projects which would relate to other work ongoing within the section.

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DESCRIPTION OF MICROWAVE-INDUCED PLASMA

In a general context, a plasma is a mixture of charged and neutral particles formed when atoms or molecules are broken down. With microwave-induced plasmas, the breakdown is usually achieved by bombarding gas molecules with high velocity electrons to produce a mixture of electrons, ions and neutral atoms. These species are very reactive and will rapidly recombine unless the breakdown process is kept going.

The role of the microwaves is to provide ongoing energy for molecular breakdown. Since it is possible to contain microwave radiation and have it resonate in small metal structures about the size of this page, it is relatively simple to maintain very intense oscillating electric fields. If the fields are strong enough, and the gas pressure is low enough, any free electrons will be accelerated to high velocities before colliding with neutral molecules. The force of the collision will frequently break apart the molecules into their constituent atoms, ions and new free electrons. These new electrons will in turn be accelerated by the microwave fields and go on to produce further ionization. An equilibrium between breakdown and recombination is quickly established and in this way the plasma is maintained by the microwaves.

Microwave-induced plasmas are very similar to those produced by radio-frequency fields. In both cases the atoms and ions typically have much lower kinetic energies than the lighter electrons. For this reason, the two types of plasmas are frequently grouped together and called low temperature plasmas.

Advantages and Disadvantages of Microwave-Induced Plasmas

Microwave energy is a particularly attractive means of generating gaseous plasmas. This is because higher degrees of ionization and dissociation can be achieved than with other types of electrical excitation. Additionally, the carrier gas remains moderately cool, even for high absorbed power levels. Microwave plasmas may also be sustained up to relatively high pressures and this makes them more adaptable to industrial application. Another important advantage is the absence of internal electrodes which are frequently a source of process contamination. This simplifies the design of clean, compact reactor vessels. Finally, the safety factor is high with this type of plasma. Personnel can readily be protected from high voltages and from stray microwave radiation.

On the negative side, there are significant technical problems in several areas. It can be difficult to produce large volumes of plasma, and if this is overcome, plasma temperature and density may not be uniform. Satisfactory operation usually requires careful tuning of the microwave system to the product load. These factors make it difficult to scale laboratory successes up to working industrial systems. Highly skilled manpower is required.

These technical difficulties result in high equipment costs. Process development work is almost always necessary in any new installation. Since this is usually undertaken on a company-by-company basis, there is little sharing of information. Turn-key production equipment is only available in the microelectronics industry. These secondary difficulties have seriously impeded the growth of industrial applications.

EXISTING AND POTENTIAL APPLICATIONS

The constituents of microwave-induced plasmas are unstable and highly reactive. They may easily be reconstituted to form new combinations and structures. Herein lies their appeal and usefulness. Conventional processes may be greatly enhanced and entirely new processes obtained using plasmas. Some specific examples and their applications follow.

Electronics Industry

The microelectronics industry is presently the largest user of low temperature plasmas in terms of equipment dollar value although power requirements are typically fractions of a kilowatt. Plasmas have found wide application by being clean, fast and dry compared to competing wet chemical processes. Plasma oxidation for photoresist removal can be done at rates of the order of 0.2 microns per minute in the presence of oxygen/2/. Exposure to the plasma lasts about 30 seconds per wafer. There is interest in developing large automated systems based on this process.

Etching of circuit patterns into silicon and gallium arsenide is another common application. Several variations are used based on keeping the semiconductor crystal at different electrical potentials with respect to the plasma. With silicon, SiF_4 gas is used to produce a complex etching reaction involving atomic fluorine/3/.

Plasmas have also been used to grow inorganic dielectric films used as dopant masks. Silicon nitride and silicon dioxide are the materials usually used. For example when a gas mixture of SiH_4 and NH_3 is used, Si_3N_4 may be formed/4/. Another possibility is to use tetraethoxysilane vapors and oxygen to form SiO_2 films/5/.

A final application in the microelectronics industry involves the deposition of organic films. The purpose of these films is to protect microcircuits from contaminants like moisture. No completely satisfactory film has been found for this application but fluorinated monomers have been used successfully with metal oxide transistors/6/.

Metal Fabricating Industry

Plasmas have been successfully used to modify the surface properties of metals. The deposition of nitrides has been used to harden gunbarrels, gears, and ball bearings using nitrogen as the working gas/7-9/. This technique has the potential to harden a wide variety of steel surfaces after machining. Carbiding may also serve this purpose and plasmas in methane have been used to carburize steel. Case hardening to a depth of one millimetre has been successful in a process which kept the steel surface at a temperature of 1000°C in the plasma. The conventional process of vacuum carburizing takes twice as long at similar temperatures/10, 11/.

It is also possible to sputter metals by keeping the metal source at a negative potential with respect to the plasma. It will then be heavily bombarded by positive ions which evaporate the metal, and deposit it on other surfaces. Sputtering chrome has been used to embellish plastic parts and at one time Varian Associates marketed on-line equipment to the automotive industry for this purpose, although this was discontinued in 1982. Plasma sputtering of titanium and copper has been used to coat architectural glass/12/.

Industries Using Polymers

It is possible to make thin polymer coatings on a variety of surfaces by introducing an organic vapor into the plasma carrier gas. The best films have been formed using dimethylpolysiloxane/13-15/, they are amorphous, pinhole-free, highly cross-linked and thermally stable. They also have high melting points and low solubility. Brittleness can be avoided by keeping film thickness to less than two microns.

By this process polymer-based materials can be highly-cross-linked to the added plasma polymer for grafting or other purposes. Applications of this type have involved fabricating reverse-

osmosis membranes, and coating paper to obtain impermeable packaging materials. Another group of applications has involved coating thin metal films. Plasma polymers have been applied to car headlamps, architectural glass, and magnetic tape to protect them from corrosion and abrasion.

The surface wettability of conventionally formed polymers may be enhanced by brief exposures to low temperature plasmas. Webs or fibers can be treated for better adherence to inks, dies, adhesives and cements/16/. These processes are important in the construction of composite materials, especially in the packaging industry.

Ceramics Industry

In the advanced ceramics industry, microwave-induced plasmas have been used to produce fine ceramic powders/17, 18/. Raw materials are vaporized in the plasma, then recondensed into a powder. Particle size is controlled by varying the cooling rate of the vapor. The small particle size of the resulting powder is important since it strongly affects the quality of the final product.

Another application has been the sintering of aluminum and uranium oxide ceramics/19, 20/. This process is still limited to the laboratory, but high speed sintering to very high densities has clearly been demonstrated. The presence of water and dopants such as magnesium oxide may benefit this process, but these have not yet been fully investigated.

Miscellaneous Applications

Microwave-induced plasmas have been used to destroy toxic wastes/21/. This has been demonstrated for PCBs, methyl bromide, ketones, and malathion. Reaction completion percentages of over 99.99992% have been obtained. However the cost and difficulty of this technique has limited its development.

Another application of possible interest to the chemical industry is the production of singlet molecular oxygen. This is an excited form of molecular oxygen with just one atom per molecule. It may be produced by striking a plasma in ordinary oxygen. Extensive interest has focused on using it as a leaching agent for lignin in wood pulp, however this has not yet been brought into production/22, 23/. Singlet oxygen is also a powerful oxidizing agent for synthesis reactions in the biomedicine and synthetic rubber industries/23/.

As a final novel example, amorphous carbon films have been formed from plasmas using hydrocarbon gases such as butane or methane/24, 25/. The resulting film is almost as hard as diamond and has been suggested as a wear-resistant film for clothing.

DISCUSSION

Reviewing the foregoing applications, it is clear that the industrial use of microwave plasmas is generally at quite an immature level of development. Existing applications typically involve low powers and low production volumes. The factors impeding further development are more to do with technical difficulty rather than technology transfer. None the less, the exception of the microelectronics industry shows that rapid growth and acceptance are possible under some conditions. To date, these conditions have involved the enhancement of quality in high added-value processes. Energy saving or cost reduction have not been very significant factors. These observations seem to limit the relevance of microwave plasmas to small specialized niches.

On the other hand research is ongoing in areas which involve mass production. For example polymer paper coating, bleaching wood pulp, or wear resistant textiles could each involve megawatts of microwave power. This combined with the falling capital cost of microwave generators implies that plasma techniques may not always remain confined to small specialized processes.

The question of what if anything the Utilization Section should be doing with microwave plasmas can be guided by the foregoing observations. Since available off-the-shelf process equipment is expensive and completely specialized for the microelectronics industry, it makes no sense to develop a demonstration capacity as we have done with radio-frequency and microwave heating. Increased use of microwave-induced plasmas requires process development, not technology transfer.

If development projects are to be initiated, there are any number of areas where contributions could be made. However, two possibilities stand out because they relate to interests already manifest in the Section. These are the sintering of advanced ceramics, and the sputtering of window coatings. Both possibilities would require further research and discussion with all parties concerned before definite project proposals could be developed. However, it is possible to outline what laboratory facilities would be required.

In addition to the microwave generators that the Section already has, any microwave plasma work would also require a specialized applicator and some gas handling equipment. The applicator would probably be a resonant, vacuum tight cavity, specially designed for the shape of the intended sample. The gas handling system would involve a vacuum pump together with pressure regulators, pressure metering instruments, and flow control valves. Supplies of specialty gases would also be necessary. Some additional instrumentation for monitoring plasma characteristics like temperature or density might also be required.

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APPENDIX A: SUMMARY OF APPLICATIONS

Rubber and Plastics

Growing polymer films
Enhancing surface wettability of conventional polymers
Grafting polymers to natural fibers

Metal Fabrication

Hardening metal surfaces
Depositing metal films on plastic and glass

Ceramics

Sintering of advanced ceramics
Production of fine ceramic powders

Chemicals

Synthesis, especially of singlet oxygen
Destruction of toxic wastes

Electronics

Etching of microcircuits in silicon and gallium arsenide
Removing photoresistive films (ashing)
Growing inorganic films as dopant masks
Applying protective organic films to microcircuits

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